Mineral Carbonates as Carbon Dioxide Sinks

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Abstract

We present the scientific basis for sequestering CO_2 in mineral form. This sequestration method makes use of the fact that carbon dioxide is not the lowest energy state of carbon. The formation of carbonates from carbon dioxide and many common magnesium or calcium bearing silicate minerals is exothermic and thermodynamically favored. Consequently, CO_2 is not the unavoidable end product of combustion. On geological time scales mineral carbonation happens spontaneously and represents an important part of the overall carbon cycle. We plan to accelerate this natural process in an industrial setting to the point where it can absorb anthropogenic CO_2 emission.

Our goal is to ensure a competitive position for fossil energy even when environmental and political pressures force drastic reductions in CO₂ emissions. In contrast to many sequestration methods, ours does not aim at buying time to phase out fossil energy. Instead it aims at a complete, environmentally sound, and economic solution with fossil fuels as the dominant world energy source. Even if world economic growth exceeds the most optimistic estimates, such a technology will assure energy availability for centuries.

We are developing an industrial process that binds CO₂ in an exothermic reaction. The result is a thermodynamically stable and environmentally benign carbonate formed from readily available mineral rocks like serpentinite or peridotite. These magnesium silicate ores are rich in magnesium, are chemically reactive, and are readily accessible in quantities that far exceed even the most optimistic estimate of coal reserves. One promising implementation is based on an HCl extraction in which magnesium is obtained as MgCl₂. The HCl is quantitatively recovered as the MgCl₂ is transformed into Mg(OH)₂. The hydroxide is carbonated in a gas-solid reaction that provides the energy consumed in recovering the HCl. The overall process is exothermic and our goal is a process design that does not require an external supply of energy. We are also considering direct carbonation of serpentinite rock. If successful, the latter process would be a net energy producer. Economically, these processes appear viable as the mining, crushing and milling operation is estimated at about \$8/ton of CO₂. Overall, we consider \$15/ton of CO₂ (0.8 to 1.5 cents/kWh) a reasonable goal. Additional work is needed to demonstrate this claim.

Introduction

In contrast to a generally held belief, CO_2 is not the lowest energy state of carbon. Instead the formation of carbonates from CO_2 and many common magnesium or calcium bearing silicate minerals is exothermic and thermodynamically favored. Consequently, CO_2 is not the unavoidable end product of combustion. On geological time scales mineral carbonation happens spontaneously and represents an important part of the overall carbon cycle. We plan to accelerate this natural process in an industrial setting to the point where it can absorb anthropogenic CO_2 emission in a cost-effective manner.

We have shown that the necessary resources exist^{2,3} and are readily accessible. We have demonstrated the basic chemistry of the process^{4,5,6,7} and have made significant progress towards an actual plant design that could reasonably achieve a disposal cost on the order of \$15/t of CO₂.⁸ At this price, our disposal scheme would be competitive with other less desirable disposal options as well as with all presently available alternative energy resources.

The Need for Sequestration

The hazards of global warming have put in question the use of fossil fuels even though they are the most reliable and most cost-effective energy resource available. Currently 85% of the world energy consumption is satisfied by fossil fuels. The resource is virtually inexhaustible. Accessible coal resources are estimated at 10,000 Gt and dwarf the annual consumption of 6 Gt of all fossil carbon. Even at greatly increased consumption, fossil energy would last for many centuries. At issue is not the availability of fossil energy, but instead the emission of carbon dioxide that results from the consumption of fossil fuels. The carbon dioxide content of the atmosphere has risen from its pre-industrial level of about 280 ppm by more than thirty percent. At present, the CO₂ level of the atmosphere exceeds 365 ppm. Most of this increase can be attributed to the burning of fossil fuels. Today, the atmospheric CO₂ level is rising at about 1.6 ppm per year while worldwide emissions from burning of fossil fuels amount to nearly 3 ppm annually. Natural CO₂ sinks account for the difference.

A scientific consensus is forming that an unabated rise in carbon dioxide levels cannot be tolerated. While it is certainly difficult to decide how much carbon dioxide is too much, it is clear that the continued use of fossil fuels could easily double the carbon dioxide level in the atmosphere by the year 2050. Considering the large fuel resources available and the expected growth in world energy demand, a tripling or quadrupling of CO₂ levels in the next century is a possibility unless carbon dioxide emissions are carefully managed. Hardly anybody would consider tripling the natural CO₂ level acceptable.

The primary concern about carbon dioxide emissions is climate change. Carbon dioxide affects the climate. Undisputedly, carbon dioxide is a greenhouse gas that is transparent to incoming sunlight, but that blocks the exit of the earth's thermal infrared emissions. Fourier¹¹ in 1827 already understood that the earth's mean temperature is about 20°C higher than it would be without greenhouse gases. Arrhenius¹² in 1896 was the first to warn about the additional greenhouse warming caused by anthropogenic carbon dioxide. From these simple facts to the prediction of global climate change is of course a big leap. Nevertheless most would agree that doubling the natural level of CO₂ is a substantial change in the environment. Climate change may not be the only effect of excess carbon dioxide in the atmosphere. Carbon dioxide is a physiologically important trace gas and thus changes in its concentration could very directly effect the ecology of biotopes. Photosynthesis is the most prominent process involving CO₂. However, carbon dioxide is also involved in maintaining blood pH. In the ocean carbon dioxide dissolved from the air could, by acidifying surface waters, interfere with coral reef formation.

Since the residence time of CO_2 in the atmosphere is long, CO_2 emissions would have to be reduced drastically in order to stabilize CO_2 levels near twice the natural level, *i.e* around 550 to

600 ppm. Model calculations by the Intergovernmental Panel on Climate Change (IPCC) suggest that emissions need to drop by about a factor three to five below the world-wide emissions in 1990 for CO₂ levels to stabilize at double the natural level. For a world population of 10 billion, the resulting per capita allowance would be about 3% of the current US per capita emission.

The need to reduce greenhouse gas emissions poses a serious threat not only to the fossil fuel industry, but also to the world and US economy. The options for reducing greenhouse gas emissions, while simultaneously providing for the growing energy demand of the world, are extremely limited. None of the competing energy resources, including nuclear, appear to be in a position to fill the gap, should fossil energy consumption need to be substantially reduced. Therefore meeting the ever growing world demand for cheap energy, while simultaneously achieving the required drastic reduction in CO_2 emissions can only be accomplished by actively preventing carbon dioxide generated in the combustion of fuels from accumulating in the atmosphere, *i.e.* by sequestration.

Sequestration is attractive, because any attempt at phasing out fossil energy is likely to fail due to the rapid growth in energy demand. As can be seen from Fig. 1, the wealth and productivity of a nation is directly related to its per capita energy consumption. Readily available, low-cost energy is an absolute necessity for the developing nations. Energy is required to achieve a decent standard of living and to overcome the political instability of a world sharply divided into rich and poor.

Figure 1 also points to the need of keeping energy costs low. The figure shows that the amount of gross domestic product (GDP) generated per kWh is only 23 cents. The cost of coal based electricity at 3 and 5 cents per kWh sets the scale. The margin for raising energy costs is small. An increase by 4 to 5 cents would strangle the economy. Wealth and an improved standard of living can only be achieved quickly and easily when the difference between the GDP and cost of energy going into the GDP is large. The price of energy must be kept low, especially in the developing countries where there is very little money available.

Fossil energy is in a unique position to satisfy the growing demand. Fossil energy is abundant and readily available, has high specific energy content, and most important, it is inexpensive.

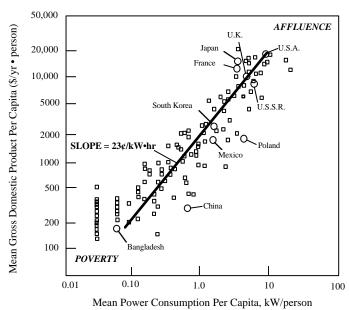


Figure 1: Per capita GDP versus per capita energy consumption for members of the United Nations. After Ref. 13.

On the other hand, the environmental impact of increased emissions of carbon dioxide from the consumption of fossil energy cannot be ignored.

Sequestration is possible and economically viable, and is currently the only realistic solution to the dilemma of CO₂ emissions. Existing technologies already demonstrate the feasibility of this approach. For example, Statoil, a Norwegian natural gas producer, injects CO₂ that is coproduced at the gas well into a deep aquifer under the North Sea.¹⁴ Ocean disposal has been studied for years. We have developed a very promising approach that disposes of carbon dioxide by chemically combining it in an exothermic reaction with readily available minerals to form carbonates. The resulting carbonates are stable solids that are known to be environmentally benign and to be stable on geological time scales. This stands in contrast to most other methods that do not appear to fully solve the long-term problem. Some, like ocean disposal, are fraught with their own environmental risks, others like deep aquifer disposal provide excellent regional solutions, but in

all likelihood will fall short of the scale required for unlimited access to fossil energy. Research into innovative methods of permanent carbon dioxide disposal capable of dealing with the full scale of the problem is needed to solve the long-term issues. We should not leave a legacy issue that future generations must deal with. New methods must be developed and must be shown to be cost-effective, safe, and environmentally acceptable. For fossil fuel to remain a viable energy option, CO₂ disposal must be permanent. If CO₂ reenters the atmosphere within a few centuries, the problem has only been postponed and not solved. Our research into its disposal as stable carbonate minerals aims at a sequestration method that can operate on a scale that allows the unrestricted use of fossil energy for at least the coming millennium.

The Mineral Carbonation Process

The concept of mineral carbonation is based on the idea that forming magnesium or calcium carbonates from most minerals is exothermic and thermodynamically favored. As a consequence, mineral carbonation has a number of intrinsic advantages over other approaches to CO₂ disposal.

- The disposal is safe. The waste products are stable and are already common in nature. They are known to be environmentally benign and non-hazardous. Most importantly there is no possibility for an accidental release of CO₂, which has proven lethal in natural disasters of comparatively small scale.
- By confining waste disposal to a mining site, we minimize the environmental impact. The
 impact is limited to a change in surface profiles. The areas involved are an order of magnitude smaller than in surface coal mining.
- Because of the thermodynamic stability and safety of the end product, disposal does not
 pose legacy problems for future generations. Other methods may require indefinite monitoring of disposal sites or could lead to a severe greenhouse problem in the future when the
 total CO₂ seepage from storage sites exceeds today's emissions.
- Our solution is permanent and complete. Resources and disposal sites far exceed the available fossil fuel reserves. The availability of this technology guarantees fossil fuels as a viable energy source. As a consequence, there will be no energy shortage for centuries to come

Most importantly mineral carbonation has the potential for a cost-effective implementation. While an above ground process may at first sight appear more costly, in practice every disposal scheme goes through a number of processing steps. If we succeed in a design that avoids the use of additional energy, the cost of the process compares favorably with that of competing approaches. Such implementations should be possible because the overall reaction is exothermic and thermodynamically favored. We consider \$15/t of CO₂ a realistic goal.

In order to demonstrate that mineral carbonation can work, we need to address the following points:

- There are common minerals for which the reaction with CO₂ to form solid mineral carbonates is exothermic and thermodynamically favored.
- These minerals can be found in concentrated mineable deposits that are sufficiently abundant to solve the CO₂ problem.
- The carbonation reaction can be performed at industrial scales and industrial speeds.
- The implementation can be made simple, fast, and energy efficient to form the basis for an economically viable industrial process.

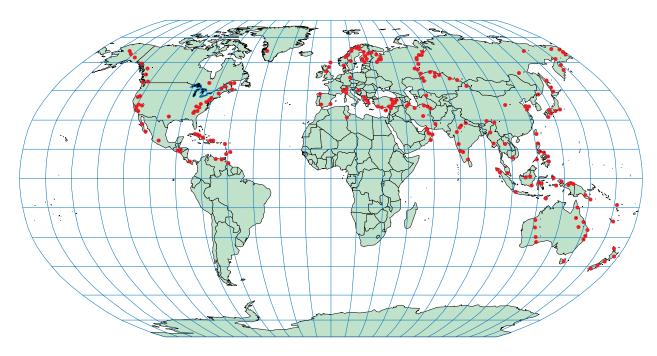


Figure 2: Locations of known peridotite or serpentinite ore bodies are marked in this map of the world. The map is drawn after Ref. 15. Many of these deposits are known to be quite large, i.e., they are measured in cubic kilometers of ore. The figure has been taken from Ref. 8.

Our present effort is focused on the last point, as we have already demonstrated the earlier points. We have shown that for the common calcium silicates and magnesium silicates, forming silica and calcium carbonate or magnesium carbonate is exothermic and thermodynamically favored. Typical enthalpies of reaction range from 50 to 100 kJ/mole. To set the scale, the heat of combustion of coal is 394 kJ/mole. At low temperatures, the carbonate is the thermodynamically favored state, *i.e.* the Gibbs free energy change of the reaction is negative. This suggests that the reaction with carbon dioxide should proceed spontaneously as it indeed does on geological time scales. It is our intention to accelerate the reaction so that it can be performed in an industrial setting.

Of all the minerals we investigated, magnesium bearing serpentinite and peridotite rocks are the most promising. They contain MgO in the form of forsterite or serpentine. The nominal MgO content of these rocks is high and easily can range to 35 to 45% by weight. In other words, to bind one ton of CO₂ requires about 2 to 2.6 tons of rock. Calcium silicates rarely exceed 15% by weight of CO₂. Chemically, the magnesium bearing rocks are quite reactive, which also stands in marked contrast to calcium silicates, which are usually very stable. The thermodynamic advantage of carbonates over magnesium silicates is demonstrated by natural carbonate formations embedded in serpentinite deposits.

The availability of serpentinite and peridotite rock is very high. Figure 2 shows a map of the world that highlights locations that are rich in these ore bodies. For more detail see Refs 2, and 3. Even without extensive prospecting that could only be justified by an economic value of a mineral, many such sites are known worldwide. In the US, many of the major sites are relatively close to the large population centers near the East and West Coasts. This makes them particularly attractive. Smaller sites also exist in other areas. For example, a site in Texas, which contains about 2.5 Gigatons of serpentinite, is still too insignificant to show up on the above maps. ¹⁶

For a deposit to be economically mineable, it needs to be large. Considering the size of modern mining equipment, any operation that does not achieve 50,000 t/day is probably too small to take advantage of the available economies of scale. The minimum lifetime of the mine is given by the

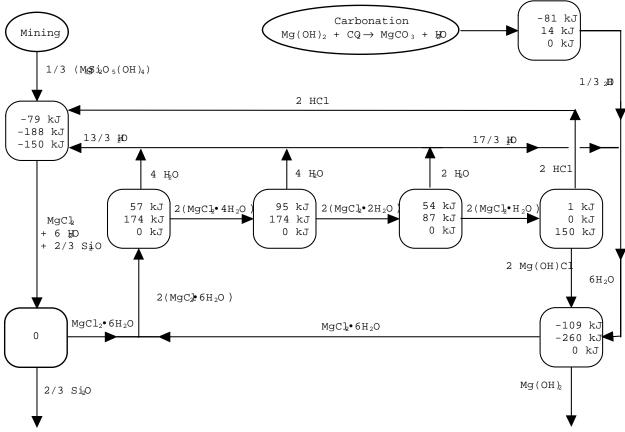


Figure 3: Outline of the chemical reaction steps in the hydrochloric acid extraction and recovery step. The boxes represent individual reactions rather than processing units. They may be combined in an implementation dependent way. The energies listed in each box refer to the enthalpy of the reaction at room temperature. The first term lists the enthalpy of the reaction with aqueous starting and final states. The second term adds to it the enthalpy of the heat of vaporization for the water involved in the reaction, and the third term adds the heat content of HCl gas relative to an aqueous solution. All numbers are referenced to room temperature and atmospheric pressure. Note too, that these energies refer to the inputs and outputs in moles. Thus they refer to the binding of one mole of CO₂. To convert these energies to heat flow rates in MW for a plant designed to match a gigawatt power plant, multiply by 6.3. (e.g. 95 kJ corresponds to 598.5 MW.)

expected lifetime of the associated processing plant which needs to be located at the mine in order to avoid transportation costs. Typical plant lifetimes should be at least 30 years. This leads to a minimum size of 0.5 Gigatons for a mineable deposit. Deposits of this size exist in many locations. We have investigated specific sites in the US^{2,3}, but a cursory survey of the literature suggests many more and even larger deposits worldwide.¹⁷

As a next step we proceeded to develop an explicit process that shows the feasibility of the carbonation of serpentine or olivine. Our initial goal was to arrive at reaction rates that would be acceptable to industrial practice. From there we shall proceed to a design that is cost effective.

To demonstrate the reaction of serpentine or olivine with carbon dioxide we have developed a two-step process. The first step is to extract the magnesium from the rock in an acidic extraction step that eventually leads to the formation of Mg(OH)₂. The hydroxide can then be carbonated in a subsequent gas-solid reaction. It is well known that serpentine and olivine dissolve readily in hydrochloric acid. The resulting hydrated magnesium chloride can be heated to release first water, and in the final step HCl, to form Mg(OH)Cl. In water, the Mg(OH)Cl dissociates into Mg(OH)₂ and MgCl₂, which is sent through the cycle again. The overall process for dissolving the mineral and forming Mg(OH)₂ is shown in Figure 3.

The carbonation of Mg(OH)₂ proceeds rapidly at 400 to 500°C and pressures as low as 6 bars. At 50 bar we have demonstrated nearly complete conversion of the Mg(OH)₂ in thirty minutes. At 6 bar we succeeded with a high degree of carbonation that occurred within a few minutes but required a long initial latency of about 100 minutes. We are still investigating the cause of this latency, but consider it likely that it can be circumvented under different experimental conditions. We conclude that the carbonation of Mg(OH)₂ is a viable process that requires fine powders (precipitates), pressures in the range of 6 to 30 bars, temperatures between 400 and 550°C, and that can be accomplished in 30 minutes or less.

All the pieces we discussed can be put together into a flow scheme that could work on an industrial scale. Thus taken together we have demonstrated a rapid process of carbonation that could treat the off gas of a large power plant. The residence times of materials in the process would be less than one hour, suggesting solid volumes of a few cubic meters per MW. We note that even though the solids and liquids may take up to an hour to move through the processing units, nowhere in the system do we store one hour's worth of CO₂. As the gas reacts continuously with the solids, the volume of gas that needs to be present at any instant of time need only be comparable in volume to that of the solids. The effective residence time of the gas can then be calculated from the volume and the rate of consumption in moles, and it tends to come out at less than one minute.

Towards A Plant Design

With regard to the overall process design, we have investigated the cost of mining, crushing, and milling the material and found this cost well within a reasonable cost budget. We have also pointed out that a simple process design of the chemical process stands a very good chance of being cost effective. Our first demonstration of a chemically viable process shows that rapid carbonation is feasible, but this first attempt is not yet cost-effective. Recently, we have performed a thermodynamic analysis of possible reaction paths which point to better, and quite likely much more cost-effective implementations.

Mining, Crushing and Milling Cost

Based on the cost of copper mining, we have estimated the cost of the mining, crushing, and milling operation to be about \$8/t of CO₂. A chemical process operating for an additional \$8/ton of CO₂ needs to be streamlined and simple. In the context of a nominal Gigawatt power plant generating 24,000 tons of CO₂ per day, a \$300 million facility, plus typical operating costs would add another \$8/t of CO₂. Based on simple dimensional arguments, we conclude that this budget is sufficient for a simple process. On the other hand, a cost of \$16/t of CO₂ adds somewhere between 0.8 to 1.5¢ to the cost of a kWh. The larger number corresponds to a conversion efficiency of 33% in a coal fired power plant. A price change of that order may well be absorbed by overall increased cost efficiency. Most importantly, it would not raise the price of fossil energy to a level that would be uncompetitive with alternative energy forms.

A coal fired Gigawatt power plant with 33% conversion efficiency generates 1000 tons of CO₂ per hour. Based on Figure 3 and an average residence time of materials in the plant of 1 hour, we find that the mass of the materials contained in the processing plant is about 3 to 4 kt. Since the residence time of the CO₂, the Mg(OH)₂, and the silica is clearly much shorter than that, this estimate is quite conservative. As long as the process equipment is dominated by containers, pipelines, *etc.*, and only a relatively small amount of mechanical equipment sufficient to move liquids and slurries from one containment vessel to the next, the total weight of the system should be of the same order. To stay below a cost of \$300 million would thus imply an equipment cost on the order of \$75 to \$100 per kg of equipment. To compare with other equipment costs, typical cars cost \$10 to \$15 per kg.¹⁸ Not surprisingly, using costs for containment vessels based on Perry's Handbook leads to vessel costs that are insignificant on the scale envisioned. A value of \$1000/m³ would imply a cost of less than \$4 million. Even a hefty cost for installation would not make a

significant difference. Of course, given the corrosive nature of some of the materials, this number may be a significant underestimate for some fraction of the vessels. Another major cost in our initial design would be in heat exchangers that could transfer the heat from all the evaporation and condensation steps implied by Figure 3. Using high heat transfer coefficients typical for evaporation units, one finds that the maximum amount of heat exchange surface would represent a cost of roughly \$50 million. Lower heat transfer rates would of course drastically raise the cost. Nevertheless, it is encouraging to find that even in this first process design identifiable costs are not so high as to make the process impractical from the start.

The implicit assumptions that went into the estimate are that the process can provide for its own energy, that gas compression is not required, and that the amount of equipment does not exceed by a large margin what is required to move liquids, slurries or powders, and heat from one reaction chamber into the next. A process directly based on Fig. 3 would quite likely violate these assumptions. For energy self-sufficiency, the endothermic HCl recovery would need to be the lowest temperature step in the cycle. This is very difficult to arrange without pressurizing steam in one place or another. Our conclusion is that we need a better, simpler process design, but that such a simple process could well stay within cost. We have demonstrated that mineral carbonation is possible; demonstrating cost-efficiency is the next step.

Developing a Better, Cost-Effective Process

Direct carbonation of serpentine at industrially viable pressures has so far reached only 30% of what is stoichiometrically possible. If the yield of this reaction can be increased it would of course offer the most direct and cost-effective way of forming mineral carbonates. We are still pursuing this avenue, but consider the outcome of this effort as uncertain.

For the chloride based processes we have developed a thermodynamical description of the $MgCl_2 + n H_2O$ melts. Typical values of n we consider are between n=1 and n=4. For the hydrated chlorides to melt under these conditions we require temperatures from $140^{\circ}C$ to $300^{\circ}C$. Steam pressures under those conditions vary from a fraction of an atmosphere to about 30 bar. Above $180^{\circ}C$, molten salts require a vapor pressure that exceeds 1 atm. Based on the available data, we were able to deduce the free energy of the salt melt as a function of temperature and water content. From the free energy of various reactions, we can now determine which processes are thermodynamically favored. As molten salts with low water content are highly reactive, we expect the thermodynamic constraints to provide a good guide as to what is practically possible in a melt.

The results can be summarized as follows. As the water content of the melt is reduced, the HCl pressure over the melt increases. This is the result of the reaction

$$MgCl_2 + H_2O \rightarrow Mg(OH)Cl + HCl.$$

For very low water content, the resulting HCl partial pressure is nearly enough to dissolve serpentine and olivine directly in the melt without adding additional HCl. The HCl partial pressure required to dissolve the mineral can again be calculated from the free energy change in that reaction. Minor pretreatment of the serpentine may suffice to make this reaction work. We are also looking at other options to raise the acidity of the melt. Even if HCl would have to be recycled through the process, it constitutes a major improvement as its lowered water content would have greatly reduced the heat inputs and outputs associated with evaporating and condensing steam. As an obstacle to this implementation we found Mg(OH)Cl is stable against repartitioning according to

$$2Mg(OH)Cl \rightarrow Mg(OH)_2 \downarrow + MgCl_2$$

unless the surrounding melt of $MgCl_2 + nH_2O$ contains at least 6 moles of water per mole of magnesium chloride (n=6). This obstacle can be overcome by reacting Mg(OH)Cl directly with CO_2 . The reaction

$$Mg(OH)Cl + CO_2 \rightarrow MgCO_3 + HCl$$

is favored in a chloride melt of any water content and CO₂ pressures on the order of a few bars.

In addition, we found that the presence of CO₂ over the chloride melt can raise the HCl partial pressure to a level that exceeds the spontaneous reaction level. The additional HCl pressure arises from

$$MgCl_2 + CO_2 + H_2O \rightarrow MgCO_3 + 2HCl$$

In a water poor chloride melt, the thermodynamic equilibrium favors a small amount of carbonate in the melt. At 20 to 30 bar of $\rm CO_2$ pressure, the calculated HCl partial pressure for this reaction is sufficient to dissolve serpentine or olivine. This dissolution reaction in turn consumes the HCl and thus causes further precipitation of $\rm MgCO_3$. In summary, a process starts in which magnesium from the mineral is dissolved and subsequently precipitated as carbonate from the melt. In this situation the chloride melt is used to speed up the reaction by providing additional reaction paths to the net carbonate reaction and is not consumed by the reaction.

We emphasize that at this point our conclusions are solely based on thermodynamical arguments and that we still have to prove that any of these reactions can be practically implemented. Our thermodynamic study has however opened a number of options that we are now ready to pursue. For more details see Ref. 19.

The last option would lead to single step process which, if proven feasible, would provide the simplification necessary to make mineral carbonation cost effective and viable.

Conclusion

We have made progress towards an economically viable implementation of mineral carbonation for the permanent and safe disposal of the carbon dioxide resulting from the combustion of fossil fuels. Once shown to be economically viable, mineral carbonation has many attractive features. It is permanent and environmentally safe, and it avoids the hazards and difficulties of storing a gas for an indefinite time scale. The method, in contrast to most others, does not just buy time for phasing out fossil energy, but instead allows for the continued and increased use of fossil energy in the future.

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